HEATS OF HYDRATION AND ABSOLUTE HEATS OF FORMATION OF AQUEOUS IONS[1]

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ABSTRACT

Accurate calculations are made for the hydration energies of the alkali halides, using the most recent data. These results, and the average of theoretical calculations made by others for the individual ions, are used to determine the most probable hydration energy of the individual ions. These in turn are the basis for calculating the absolute enthalpy of formation of aqueous H^+: 98.6 kcal/g-equiv. A Born-Haber cycle can then be used to calculate the hydration energy of any other ion for which the enthalpy of the gaseous ion is known.

HEATS OF HYDRATION OF THE ALKALI HALIDES

Although computations of the heats of hydration at infinite dilution of the alkali halides have already been made, the accumulation of more accurate data warrants a recalculation. The data come from critical compilations by the National Bureau of Standards (1952, 1965). The results of these calculations are given in table 1. The very high precision and internal consistency of these data can be demonstrated by obtaining the differences between values of adjacent columns and rows, thereby obtaining differences for halides and alkalis, respectively.

TABLE 1

Standard enthalpies of solution of gaseous ionic alkali halides in kcal/mole at 25°

	F^-	Cl^-	Br^-	I^-
Li^+	−243.4	−210.6	−202.4	−195.8
Na^+	−217.1	−184.4	−176.2	−169.6
K^+	−197.1	−164.3	−156.2	−149.5
Rb^+	−191.1	−158.2	−150.2	(−143.5)[a]
Cs^+	(−183.3)[b]	−150.5	−142.3	−135.6

[a], [b]Based on ΔH_f° of −78.2 and −129.1 for RbI(c) and CsF(c), respectively (reason for choice explained in text).

The differences in hydration energies of adjacent halide and alkali metal ions are given in table 2. The figures in parentheses are obtained by using the assumed values for enthalpy of formation of RbI and CsF given in table 1. By so doing, the differences between the ions involved are consistent with differences resulting from use of the other compounds. For example, the figure −183.3 for CsF gives consistent values for both F^-–Cl^- and Rb^+–Cs^+. This close agreement and internal consistency, in fact, argue for a revision of the thermodynamic data for RbI and CsF.

HYDRATION ENERGIES OF THE INDIVIDUAL IONS

Given the total energy of hydration in table 1, and the differences in table 2, it would be easy to calculate the energy of hydration of each of the individual ions if the value for any one ion were known accurately, or if an accurate ratio were known for any two halide or alkali ions. (The calculation of a ratio would appear to be the most promising approach to exact calculations, because common errors

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might be more apt to cancel in taking the ratio.) However, such exact calculations have not yet been achieved.

Many attempts have been made to calculate the energies of hydration of the individual ions. A summary of the calculated values is given in tables 3 and 4. These involve several different theoretical approaches and assumptions. It is possible, therefore, that errors in the calculations will almost cancel when the average is taken. This average of the calculated values is given in tables 3 and 4. The differences between these averages are very close to the experimental differ-

TABLE 2

Differences in hydration energies of halide and alkali metal ions

	F^-–Cl^-	Cl^-–Br^-	Br^-–I^-	Li^+–Na^+	Na^+–K^+	K^+–Rb^+	Rb^+–Cs^+
	32.8	8.2	6.6	26.3	20.0	6.0	(7.8)
	32.7	8.2	6.6	26.2	20.1	6.1	7.7
	32.8	8.1	6.7	26.2	20.0	6.0	7.9
	32.9	8.0	(6.7)	26.2	20.1	(6.0)	(7.9)
	(32.8)	8.2	6.7				
Ave.	32.8	8.1	6.7	26.2	20.0	6.0	7.8

TABLE 3

Caluculated hydration energies for the alkali ions

	Li^+	Na^+	K^+	Rb^+	Cs^+	Source
	136	114	94	87	80	Bernal & Fowler, 1933
	133	115	90	81	73	Eley & Evans, 1938
	121.2	94.6	75.8	69.2	62	Latimer, et al., 1939
			75		53	Verwey, 1942
	125	98	78			Mishchenko, 1935
	139.8	107.9	84.7	78.5	75.1	Azzam, 1960
		121	81.1			Ishida, 1960
	121.0	92.0	78.0	74.0	66.0	Izmailov, 1963
	127	101	81	75	67	Vasil'ev, et al., 1960
	113.2	95.8	74.6	67.4	61.3	Lagunov, 1958
Average	127.0	104.4	81.2	76.0	67.2	
	Average adjusted to difference in Table 2					
	128.1	101.9	81.9	75.9	68.1	
	Above plus 2.7 (see text)					
	130.8	104.6	84.6	78.6	70.8	

ences shown in table 2, so, to this extent, the average values are recognized as being internally consistent. In the next lower horizontal row, these averages are adjusted so that their differences agree with table 2 but the total for their sum constant remains the same, e.g., 455.8 for alkalis.

It should be noted, however, that the sums of the hydration energies of the individual ions fall short of the actual hydration energies of the salts given in table 1, as do also several of the individual calculated values making up the averages. This apparently results from insufficiencies or errors present in most of the methods for calculation of hydration energy. All the adjusted average values are

low by about the same amount. Because it is impossible to decide whether the error lies with the alkali or with the halide ions, a constant amount, 2.7 kcal, is added to each, such that the sum of hydration energy of cation and anion shall equal the experimental value given in table 1. The figures in the lowest horizontal rows of tables 3 and 4 are then the most probable values for the hydration energies of the individual ions at infinite dilution, and the sums of these agree quite well with the experimental values in table 1.

TABLE 4

Calculated hydration energies for the halide ions

	F^-	Cl^-	Br^-	I^-	Source
	97	65	57	47	Bernal & Fowler, 1933
	91	59	52	45	Eley & Evans, 1938
	122.6	88.7	81.4	72.1	Latimer, et al., 1939
	122			72	Verwey, 1942
		88	77	66	Mishchenko, 1935
	106.7	71.7	68.0	63.7	Azzam, 1960
		67.4			Ishida, 1960
	107.0	79.0	72.0	64.0	Izmailov, 1963
	116	84	76	67	Vasil'ev, et al., 1960
	113.4	81.5	74.5	65.3	Lagunov, 1958
Average	109.4	76.0	69.7	62.5	
	Average adjusted to difference in Table 2				
	109.7	76.9	68.8	62.1	
	Above plus 2.7 (see text)				
	113.4	79.6	71.5	64.8	

ABSOLUTE HEATS OF FORMATION FOR HYDROGEN ION AND OTHER IONS

The previous calculations do not merely give the heats of hydration of the alkali metal and halide ions, but put us in position to determine the absolute heats of formation of these and other aqueous ions, and also the heats of hydration of other ions.

It is customary to assume that the heat of formation of H^+ ion is zero at unit activity. This, of course, results in a constant unknown error in the heats of formation of other ions. Thus the relative enthalpy change for the reaction

$$Na(s) \rightarrow Na^+ \ (a=1)$$

is given (National Bureau of Standards, 1965a) as -57.4 kcal/mole, whereas the absolute enthalpy change is this number plus a constant, i.e., $-57.4+A$.

However, if one calculates the heat of formation of a salt in solution by adding the values (relative to hydrogen) of both anion and cation, one obtains the absolute heat of formation of the acqueous salt. It follows then that the correction for anions must be $-A$, since the constant cancels from the sum. Thus, the absolute enthalpy change for the reaction

$$\tfrac{1}{2}\ Cl_2(g) \rightarrow Cl^- \ (a=1)$$

is $-40.0-A$.

Once the heat of solution of any gaseous ion is known, the value of the constant A may be determined by a Born-Haber cycle. It is given by

$$A = \mp \Delta H_f^\circ \text{ (aq. ion)} \pm \Delta H_f^\circ \text{ (gaseous ion)} \pm \Delta H_{soln.}$$

where the plus sign applies to positive univalent ions and the negative sign to

negative univalent ions. The average of the calculations using all the alkali metal and halide ions gives 98.6 kcal per equivalent. In other words, this gives the absolute standard enthalpy change for the reaction

$$\tfrac{1}{2}\ H_2(g) \rightarrow H^+(aq.)$$

a value of 98.6 kcal/equiv. This agrees with other estimates and calculations (Halliwell and Nyburg, 1963; Noyes, 1964; Stokes, 1964). The absolute enthalpy of formation of Cl^- (aq.) in the standard state is then -138.6 kcal/mole.

HEATS OF SOLUTION OF OTHER IONS

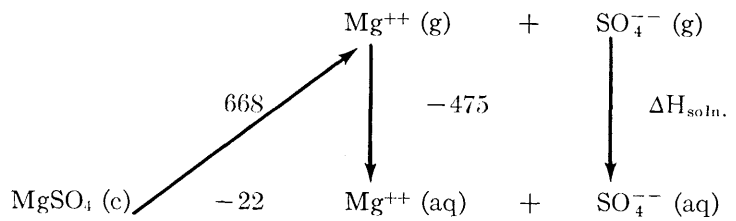
The evaluation of the absolute heats of formation of aqueous ions (by use of the constant, A, and the heat of formation relative to hydrogen) then allows the easy calculation of the heat of hydration of any other ion whose enthalpy may be determined in the gaseous state.

In the following equation, Z is the charge on the ion, and the positive and negative signs apply to positive and negative ions, respectively.

$$\Delta H^\circ_{soln.} = \Delta H^\circ_f \text{ (aq. ion)} - \Delta H^\circ_f \text{ (gas. ion)} \pm 98.6\ Z$$

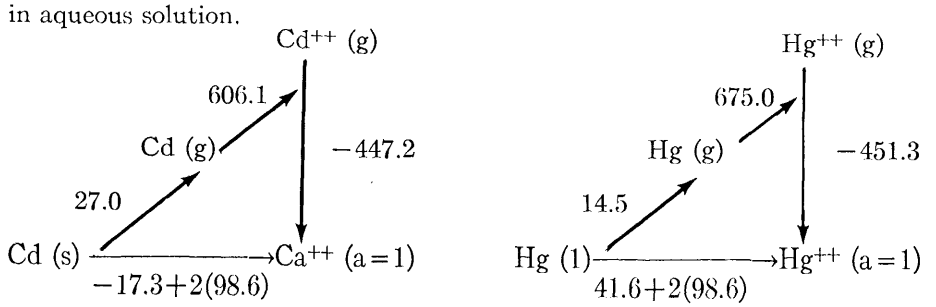
The accuracy of this computation is limited by the accuracy of the division of hydration energy between the alkali and halide ions (and consequently by the constant A), and by the accuracy of measurement of the enthalpies of formation of the gaseous and aqueous ions.

It is also possible to proceed from lattice energies of ionic crystals. This approach is especially useful when the lattice energy can be accurately estimated (Kapustinskii, et al., 1943, 1949, 1956), although the heats of formation of the gaseous ions are not so accessible. As an example, the sulfate ion may be used.



The heat of solution, $-\Delta H_{soln.}$, of the sulfate ion can be calculated to be 215 kcal/mole.

Such calculations make it possible to more easily interpret the differences in activity of the various elements. For instance, one can compare Cd^{++} and Hg^{++} in aqueous solution.



It can be seen that the energies of hydration of the Cd^{++} ion and the Hg^{++} ion are almost the same. The more noble character of mercury is due solely to its high ionization potential, because the low heat of vaporization tends to make it more active.

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